Deposition and Characterization of Chemically Synthesized Copper Indium diSelenide (CIS) Thin Films for Solar Energy Applications

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Abstract: ***High energy band gap CIS thin films have been generated for the design of photovoltaics/solar cells using chemical bath deposition technique. The deposition was based on the reaction between aqueous solutions of CuCl2.2H2O, InCl3.4H2O and Na2SeSO3, in an alkaline medium of NH3(aq), TEA and EDTA being the complexing agents. Optical properties of the deposited thin films were measured with the aid of Avantes UV-VIS-NIR spectrophotometer in the wavelength range 200-900nm. Also, the electrical properties (reflection, transmission and absorption data) were obtained using Four Point-Probe machine. Results obtained from the optical and electrical characterization of the films indicate that CIS can be potentially used as window layers in hetero-junction solar cells because they exhibited high band gap energy and low electrical resistivity which are required properties for window layers.***

Keywords: CIS, Thin films, optoelectronic, solar cell, fabrication

1. Introduction

The current trends failure in the generation of enough electricity from hydro-plants and thermal plants suggest the important role of solar energy in future energy production. Solar power seems strange or futuristic, but it is already quite common as one might have a solar-powered quartz watch on his/her wrist or a solar-powered pocket calculator, in fact, many people have solar-powered lights in their garden. The American space agency (ASA) has even developed a solar-powered plane [4]. The probable candidates in the field of photo electrochemical solar cells are CdS and CdSe [2]. Recently, work on chemically deposited CdSe and Sb_2S_3 films with incorporation of WO_3 has shown appreciable conversion efficiency and stability in photo electrochemical solar cell configuration [11]. It is only 10 years since chemically deposited thin films have found their active role in thin film solar cells. In 1990, a thin layer of chemically deposited CdS thin film was integrated into a structure Mo/$CuInSe_2$/CdS/ZnO producing approximately 11 % conversion efficiency. Later improved cell design resulted in record efficiencies greater than 17% [7]. Theoretical calculations have shown that the thickness of CdS film should be as small as possible for better cell efficiency. This could be attained easily by Chemical Bath Deposition (CBD) technique. The fabrication of heterojunction solar cells using chemically deposited Sb_2S_3 thin films on p(Si)/p(Ge)/p(lnP) wafers has been reported recently. Nair and his group have many publications on this simple technique of CBD [9]. Lokhande in 1991 mentioned about more than 35 compounds prepared using this technique. All these hint that the number of materials that are deposited by CBD will increase significantly in the nearest future. In the field of CBD, the Photovoltaics laboratory at Cochin University of Science and Technology in India has also contributed significantly. The first CIS/CdS trial thin film solar cell in which both the n-type and p-type materials were prepared using CBD technique comes to the credit of this material. Lakshmi in 2001 also succeeded in depositing elemental selenium thin films from an acidified bath of sodium selenosulfate. Scientists refer to silicon solar cells as first generation and this classification largely differentiate them from the modern technologies types called second and third generation solar cells. Demand for the generation of electricity from renewable energy sources has been on a continuous increase for centuries due to rapid depletion of fossil fuel sources which is not replenish able. Generation of electricity from solar photovoltaic is still quite expensive and puts heavy demand on production of high purity silicon. Solar cells made from silicon are very expensive due to high cost in process of purification from sand and wafer production. The increase in demand for solar energy as the alternative to present power source which is cheapest and safer is obtainable via production of CIS films through CBD technique.

2. Experimental Details

The starting chemicals used in this study were copper (II) chloride dihydrate ($CuCl_2.H_2O$) as the source of Cu^{2+} and Triethanolamine (TEA) as a complexing agent, sodiumselenophite (Na_2SeSO_3) as a source of selenium ion (Se^{2-}) and Indium(III)chloride tetrahydrate ($InCl_3.4H_2O$) as a source of indium ion (In^{3+}) whereas Ethylene Ditetraamine acid (EDTA) as a complexing agent for In^{2+} in the reaction mixture of both. Ammonia (NH_3) was used to adjust the pH of the solution. The sodium selenosulphite was prepared by refluxing 9.0 g of selenium power with approximately 15.0g of anhydrous sodium sulphite (Na_2SO_3) in 200ml of distilled water for 6 hours at 80°C thereby making 0.2 M of Na_2SeSO_3.

CIS thin films were synthesized on glass substrates by CBD technique at 85°C. Prior to the growth, the glass substrates were degreased in HCl for 24 hours, washed with detergent, rinsed with distilled water and dried in air. The deposition of CIS thin film was based on the reaction between aqueous solution of $CuCl_2.2H_2O$, $InCl_3.4H_2O$ and Na_2SeSO_3, in an alkaline medium of $NH_{3(aq)}$ and TEA and EDTA as complexing agents. For deposition, a reaction bath (100 mls beaker) was used. 10 mls of $CuCl_2.2H_2O$ were measured into a 50ml beaker using burette, 5mls of TEA were added to it,

$InCl_3.4H_2O$ were measured into a 50mls beaker using burette 5 mls of 0.5mol trisodium citrate were then added. 20mls Na_2SeSO_3, 20 mls $NH_{3(aq)}$ were added to the solution. The mixture was topped to 90mls level by addition of distilled water and stirred gently to ensure uniformity of the mixture. Copper(II)chloride dihydrate ($CuCl_2.2H_2O$), Indium (III) chloride tetrahydrate ($InCl_3.4H_2O$) and sodium selenosulphite (Na_2SeSO_3) were the sources of Cu^{2+}, $In^{3+}$and Se^{2-} respectively. The deposition process was carried out at different deposition times of 3, 6, 9, 12 and 15 hours in order to determine the optimum condition for the deposition of CIS thin film. The experiment was conducted at 85°C temperature. Two cleaned glass substrates were vertically immersed into the chemical baths with the help of a suitable designed substrate holder as shown in Figure 1. After the deposition, the substrates containing the deposited films were removed, allowed to dry in open air at room temperature, one labeled CIS as-deposited and the other substrate annealed at 450°C in an electric furnace then labeled CIS annealed. The deposition temperatures and the pH (11.5-11.3) were monitored with Mettler Toledo AG 8603 pH meter. Table 1shows the chemical bath compositions for the deposition of the thin films.

Table 1: Chemical Bath Compositions for the deposition of CIS Thin films

Baths	Cu	In	Se	pH
	Concentration (M)			
S_1	0.3	0.1	0.2	11.50
S_2	0.3	0.2	0.2	11.40
S_3	0.3	0.3	0.2	11.30

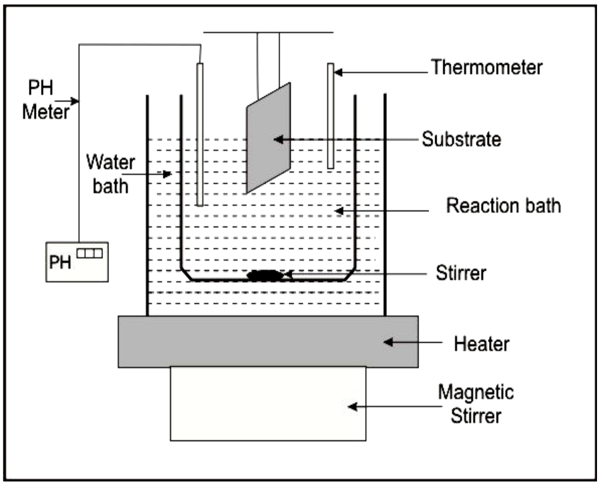

Figure 1: Schematic experimental set-up for Chemical Bath Deposition of CIS

3. Results and Discussion

Optical properties were measured with the aid of Avantes UV-VIS-NIR spectrophotometer in the wavelength range 200-900nm. Also, the electrical properties (reflection, transmission and absorption data) were obtained using Four Point-Probe machine. Sheet resistance, resistivity and conductivity of the deposited thin films were calculated.

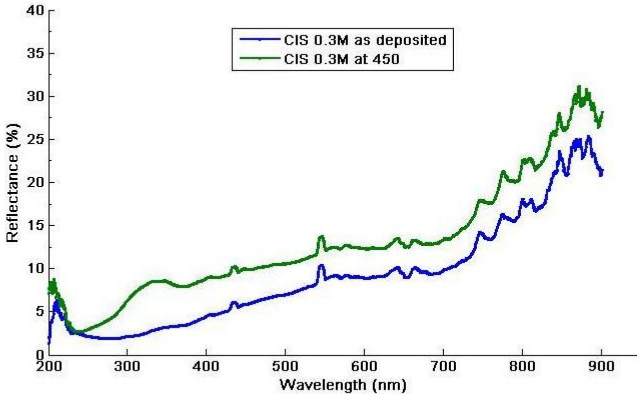

Figure 2: Graph of reflectance against wavelenght for CIS

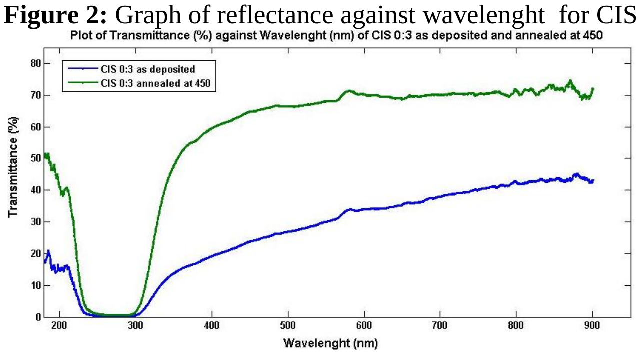

Figure 3: Graph of transmittance against wavelenght for CIS

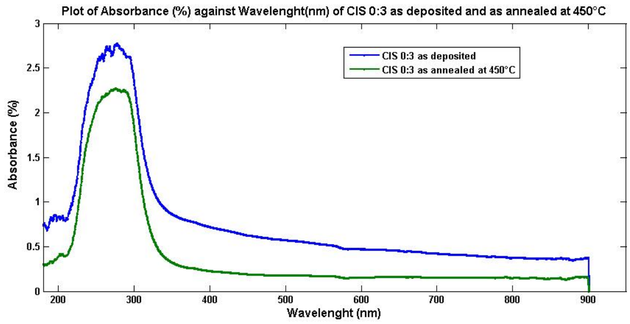

Figure 4: Graph of absorbance against wavelenght for CIS

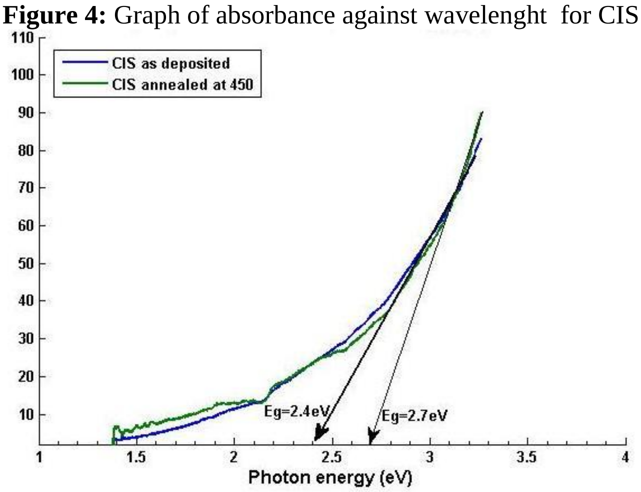

Figure 5: Graph of $(\alpha h\nu)^2$ against photon energy in eV for CIS

Table 2: Summary of the electrical results of CIS

Samples	Resistivity (Ωm)	Conductivity (Ωm^{-1})	Sheet resistance, R_s (Ω/m^2)
CIS as-deposited	2.05×10^{-3}	4.878×10^{3}	1.027×10^{-1}
CIS Annealed	4.37×10^{-4}	2.288×10^{3}	2.186×10^{-2}

4. Discussion

The optical analyzes (reflection, transmission and absorption data) were accomplished by using Avantes UV-VIS-NIR spectrophotometer in the range 200-900nm. Optical measurements are of importance in analyzing semiconductors because the effects deal with transitions between bands and or energy levels inside the band gap. Figure 2 shows the reflectance graph of CIS thin films which was found to be about 6-27% and 9-33% for the as-deposited and annealed samples. Reflectance becomes very small around 250 nm. It is observed that the annealed sample has the highest peak to the as-deposited. This is in agreement with the work of [1] who reported chemically deposited copper selenide thin films. [10] also reported similar behaviour for $Cu_{2-x}Se$ thin films prepared by CBD. It was observed that average reflectance was below 40% for the annealed film and below 35% for as-deposited thin film. Transmittance is obtained to be between 17-45% and 48-75% for the as-deposited and annealed films in the wavelength range 200-900 nm (Figure 3). A gradual decrease in transmittance is generally observed in the lower region (220-300 nm) then increases steadily and this may be due to absorption by free carriers in the degenerate films. Annealed samples had highest transmittance above 600 nm (i.e. in the ultraviolent visible electromagnetic spectrum range). Below 300 nm there was a sharp fall in the percentage transmittance of the films, an indication of a strong increase in absorption [5]. This is attributed to the increase in fundamental absorption as photon striking increases with increase in carrier concentration [6]. Figure 4 shows the absorption spectra for the films and the absorption was around 2.8% with wavelength 300 nm. In the near infrared, the transmittance was observed to be less dependent on wavelength above 700 nm. Visible region of wavelength becomes almost consistent in the infrared region. This agrees with the report of [3]. who deposited ZnSe on quartz using vacuum evaporation technique. The band gap energy of the films ranged from 2.4-2.7eV as deduced from the extrapolated curve in Figure 5. However, this kind of deviation was reported by [12] where CdTe film was grown and the band gap energy of 2.8eV was obtained instead of 1.5eV. The researchers also obtained 2.98eV for CdS thin film instead of 2.4eV and it was concluded that this makes the film a better window material in an n-CdS/p-CdTe heterojunction solar cell.

The resistivities of the thin films from Table 2 are 2.05×10^{-3} Ωm and 4.37×10^{-4} Ωm for as-deposited and annealed at 450^0 C respectively and their respective conductivities are 4.878×10^3 Ωm^{-1}, 2.288×10^3 Ωm^{-1}. [13] obtained similar sheet resistivity measurements for ZnS were using Van der Pauw technique in the order of 10^{-1} Ω cm to 10^{-2} Ω cm and electrical conductivity of 10^2 to 10^3 $(\Omega\ cm)^{-1}$.

5. Conclusion

CIS thin films are semiconducting materials which are deposit-able by chemical bath deposition which are useful in solar energy absorbance for direct conversion of solar energy to electrical energy. They can be potentially used as window layers in hetero-junction solar cells because they exhibited high band gap energy and low electrical resistivity which are required properties for window layers. They are recommended as good materials for antireflection coatings, solar cell absorbers, thermal control and photosynthetic coatings due to their low reflectance properties.

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